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(21) International Application Number: PCT/US97/16325 (22) International Filing Date: 17 September 1997 (17.09.97) (30) Priority Data: 08/721,742 27 September 1996 (27.09.96) US (71) Applicant: SOUTHWEST RESEARCH INSTITUTE [US/US]; 6220 Culebra Road, San Antonio, TX 78238-0510 (US). (72) Inventor: WELLINGHOFF, Stephen, T.; 7718 Benbrook, San Antonio, TX 78250 (US). (74) Agent: SIGALOS, John, L.; Suite 820, 13760 Noel Road, Dallas, TX 75240 (US).		(81) Designated States: CA, JP, MX, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: METAL OXIDE COMPOSITIONS AND METHODS (57) Abstract Metal oxide and metal oxide-silica nanoparticles are disclosed wherein the surfaces thereof are complexed with a polymerizable, biocompatible, heterocyclic base. Polymerizable compositions are prepared by loading such nanoparticles into acrylate based monomer matrices, which compositions can then be photocured into X-ray opaque, transparent or translucent solids. Methods are disclosed for forming such complexed nanoparticles and compositions and for using such compositions as medical or dental restoratives.		

indium, tin, and the like it will be described in connection with tantalum. Tantalum is particularly desired for dental and medical uses since it will provide X-ray opaque materials necessary for subsequent review of the treated site; i.e., tooth or bone, by dentists and doctors.

- 5 These tantalum nanoparticles are prepared as set forth in U.S. Patent No. 5,372,796 by ester exchange of tantalum oxide with an acid such as formic acid.

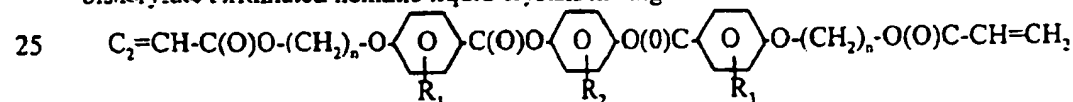
For this invention it is important that such nanoparticles be non-interacting without high surface acidity. High surface acidity is detrimental for dental applications. Accordingly, a polymerizable, biocompatible, heterocyclic base that can complex the acid
 10 sites on the surface of the tantalum oxide nanoparticles is admixed therewith. It is preferred to use alkene terminated imidazoles and phosphates for this purpose with specific examples being 1-vinyl imidazole (VIM) and the phosphonated acrylic ester, PHEMA, formed by reacting diethylchlorophosphate with hydroxyethyl methacrylate (HEMA) in the presence of triethylamine in ether. Such PHEMA has the formula:



It will be evident that other like polymerizable imidazoles and phosphates can be utilized with, for example, compounds in which a liquid crystal moiety of the type set forth below is inserted between the alkene and imidazole or alkene and phosphate moieties.

Such complexed tantalum oxide nanoparticles with imidazole or phosphate
 20 termination have no particle intraction or network formation and have enhanced coupling with the matrix resin(s).

As to the matrix monomers there are used photopolymerizable, acrylate based monomers, particularly those useful in dental applications. Particularly preferred are the bisacrylate terminated nematic liquid crystals having the formula:



In this formula n is a C_6 to C_{12} substituted or unsubstituted alkyl group, R_1 and R_3 are H or a methyl group and R_2 is a bulky group (a group of providing steric hindrance), such as a tertiary butyl group and the like. This large group size "mismatch" between the central
 30 aromatic group and the two surrounding aromatic groups is required to achieve in the final